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ARTICLE

Experimental Investigation on Phase Equilibria of Mo-Ru-Ti Ternary System

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Abstract: The isothermal sections of the Mo-Ru-Ti ternary system at 1100 and 1300 °C were established using electron probe microanalysis and X-ray diffraction techniques. The results indicate that there are three three-phase regions at 1100 °C isothermal section and two three-phase regions at 1300 °C isothermal section; the σ-Mo_5Ru_3 phase is stabilized to 1100 °C and forms a small single-phase region with the addition of Ti. The β(Ti, Mo) phase extends from Mo-rich side to Ti-rich side and dissolves a lot of Ru at 1100 and 1300 °C. The phase relationship of Mo-Ru-Ti system will provide basic experimental data for the thermodynamic database of titanium alloys.

Key words: Mo-Ru-Ti; phase diagram; titanium alloys; electron probe microanalysis

Due to low densities, excellent resistance to elevated temperatures, the titanium alloys are extensively used as the heat and corrosion resistant materials in the aerospace, shipbuilding, petrochemical industries[1-3]. However, the creep resistance and oxidation resistance of Ti-based alloys fall sharply at high temperatures, which restrict the development of the Ti-based alloys[2]. To solve the disadvantages above, titanium and its alloys are improved by adding alloying elements, such as Nb, Ru, Hf, Mo and Co[3-11]. The element Mo can refine the grain, improve the hardenability and thermal strength, maintain sufficient strength and creep resistance at high temperature[7, 11]. The element Ru has become the critical element for the superalloys. The addition of Ru promotes the microstructural stability and improves the creep resistance. Also, Ru can enhance high temperature stress rupture properties of the superalloys[8-10]. The amount of the refractory elements is supposed to be controlled accurately because excessive addition will introduce detrimental phases and then damage alloy performance. Therefore, the investigation on phase equilibria of Mo-Ru-Ti system is required to give essential information about phase stability and structure properties of the Ti-based superalloys. However, so far, little experiment investigation about the phase equilibria of Mo-Ru-Ti has been reported. It is necessary to investigate the phase equilibria of the Mo-Ru-Ti ternary system.

Three binary systems, Mo-Ru, Mo-Ti, and Ru-Ti which constitute the Mo-Ru-Ti ternary system, are shown in Fig.1.

Kleykamp[12] investigated the constituent of Mo-Ru binary system at 800~2000 °C and found that the σ-Mo_5Ru_3 phase exists at 1143~1915 °C. Rand[13] and Cornish[14] et al evaluated the Mo-Ru binary system, but the σ-Mo_5Ru_3 phase was not taken into account in calculation, thus forming the metastable phase diagrams. Later, Oh et al[11] reassessed the Mo-Ru binary system and paid attention to the thermodynamic description of the σ-Mo_5Ru_3 phase. The Mo-Ru phase diagram assessed by Oh et al[11] was applied in this work. There are only two solid phases of Mo and Ru,

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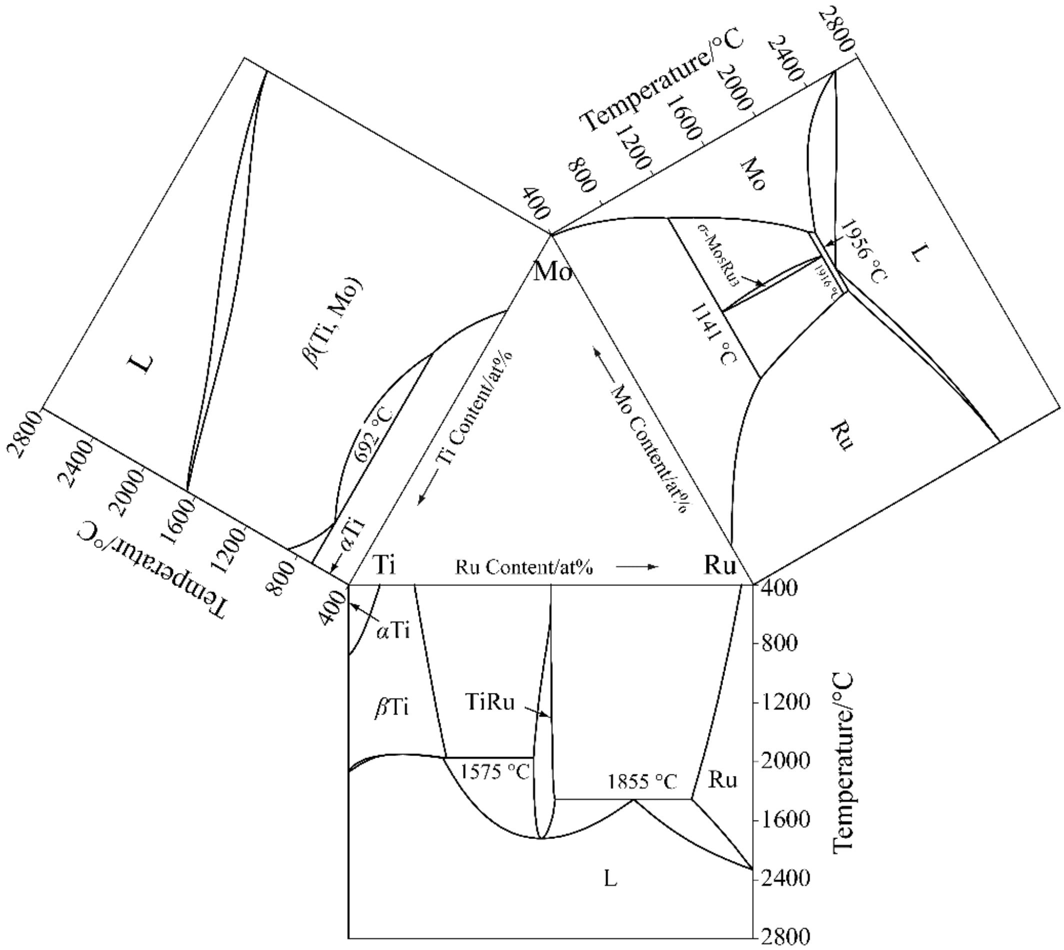

Fig.1 Binary phase diagrams constituting the Mo-Ru-Ti ternary system[11,20,26]

and one intermediate phase σ-Mo_5Ru_3 existing in the Mo-Ru system[11]. The σ-Mo_5Ru_3 phase which occupies a narrow composition range around 36.8 at%~38.5 at% is obtained from peritectoid reaction of Mo+Ru↔σ-Mo_5Ru_3 at 1916 °C while it decomposes by the eutectoid reaction of σ-Mo_5Ru_3↔Mo+Ru at 1141 °C.

For the Mo-Ti binary system, Hansen et al[15] investigated the solidus curve and determined temperatures of incipient melting by metallographic examination of quenched specimens. In addition, based on micrographic and X-ray analyses, they determined the phase boundary between bcc and hcp in the Ti-rich region. Duwez[16], Flower et al[17], and Williams[18] also measured the phase boundary and obtained the similar results. Murray[19] made a thorough review and an assessment of the Mo-Ti system. Later, Shim et al[20] evaluated the Mo-Ti and Mo-Ti-C phase diagrams. Barzilai et al[21] investigated the Mo-Ti phase diagram by ab-initio calculations and they predicted that the β-phase is stable over a wide concentration range. The Mo-Ti phase diagram assessed by Shim[20] was applied in this work. Two solid phases exist in this system, one is the αTi phase and the other is an infinite solid solution phase of β(Ti, Mo).

Murray[22] evaluated the Ru-Ti binary system using the symmetrical regular solution model and Wagner-Schottky model (Ru, Ti) (Ti, Va) for RuTi. Kaufman and Bernstein[23] used the regular solution approximation to model the phase equilibria, and treated the TiRu phase as the stoichiometric compound. Liou and Wilkes[24] predicted the effect of radiation induced disorder on the stability range of TiRu. Later, Mazhuga et al[25] reassessed the Ru-Ti system and also treated the TiRu phase as the stoichiometric compound. In 2009, Gao et al[26] optimized the Ru-Ti binary system and applied the two-sublattice model in the TiRu phase with a composition range from 49.0 at%~54.3 at% Ti. The Ru-Ti system assessed by Gao et al[26] was used in this work. The Ru-Ti system has only one intermediate-phase TiRu, which melts congruently at around 2120 °C. The eutectic reaction of L↔Ru+TiRu and the peritectic reaction of L+TiRu↔βTi occur at about 1855 and 1575 °C, respectively.

Table 1 Crystal structures of each phase in the Mo-Ru-Ti ternary system[11,20,26]

System	Phase	Pearson symbol	Space group	Prototype	Structure type	Ref.
Mo-Ru	Mo	cI2	Im-3m	W	A2	[11]
	σ-Mo_5Ru_3	tP30	$P4_2/mnm$	σCrFe	$D8_b$	[11]
	Ru	hP2	$P6_3/mmc$	Mg	A3	[11]
Mo-Ti	αTi	hP2	$P6_3/mmc$	Mg	A3	[20]
	β(Ti, Mo)	cI2	Im-3m	W	A2	[20]
Ru-Ti	αTi	hP2	$P6_3/mmc$	Mg	A3	[26]
	βTi	cI2	Im-3m	W	A2	[26]
	TiRu	cP2	Pm-3m	CsCl	B2	[26]
	Ru	hP2	$P6_3/mmc$	Mg	A3	[26]

All the stable solid phases and their crystal structures in the three binary systems are summarized in Table 1.

The Ti-based superalloys are one of the most competitive materials which are widely applied in high-temperature areas. Investigating the phase equilibria of Mo-Ru-Ti at high temperatures is more important. Therefore, the temperatures of 1100 and 1300 °C were chosen. The present work aimed to experimentally investigate the phase equilibria of the Mo-Ru-Ti ternary system at 1100 and 1300 °C using electron probe microanalysis and X-ray diffraction techniques. The result of the experimental investigation will provide useful information for the development of Ti-based high-temperature alloys.

1 Experiment

All the raw materials used in this work were high-purity molybdenum (99.9 wt%), ruthenium (99.9 wt%), and titanium (99.9 wt%). The semi-micro analytical balance with an accuracy of at least 0.5 mg was used to measure the required mass of the elements. The mass loss of the samples was usually less than 1% during the whole preparation procedure, which was assumed to make no significant effect on the sample composition.

All the bulk alloys were prepared in the form of atomic fraction (at%) and the chemical composition of alloys and phases was described using atomic percent. The bulk alloys, each about 20 g, with a nominal composition were prepared by non-consumable tungsten electrode arc-melting on a water-cooled plate in an argon atmosphere. The arcing and getter materials were the titanium ingot.

Each alloy was re-melted at least five times to promote complete mixing and melting, thus obtaining the homogeneous ingots. Afterwards, the specimens for heat treatment were cut into small pieces by a wire-cutting machine. The samples were cleaned by an ultrasonic cleaner and then wrapped with the titanium foil to prevent the direct contact with the quartz ampoules. Later, the samples and yttrium filings were sealed into quartz tubes evacuated and back-filled with high-purity argon gas. The function of the yttrium filings was to absorb oxygen at high temperature. The specimens were annealed at 1100 °C for 50 d and 1300 °C for 15 d to reach phase equilibria. Subsequently, the specimens were quenched, mounted, grinded, and polished.

Electron probe microanalysis (EPMA, JXA-8100R, JEOL, Tokyo, Japan) was performed to observe the microstructure and to analyze the equilibrium composition of the alloys. Pure elements were used as standards and the measurements were carried out at a voltage of 20 kV and a current of 1.0×10^{-8} A. The crystal structures were characterized by the X-ray diffraction (XRD) measurements which were performed on a Philips Panalytical X-pert diffractometer (Bruker Daltonic Inc., Massachusetts, the United States) with Cu Kα radiation at 40 kV and 40 mA. The scanning range of 2θ was from 20° to 90° at a step size of 0.0167°.

2 Results and Discussion

2.1 Microstructure

Fig.2 shows the typical back-scattered electron (BSE) images of ternary Mo-Ru-Ti alloys annealed at 1100 and 1300 °C for different time. The three-phase equilibrium microstructures are shown in Fig.2a and 2b and two-phase equilibrium microstructures are shown in Fig.2c~2f. The corresponding XRD results are presented in Fig.3.

Fig.2a shows the BSE image of the $Mo_{55}Ru_{30}Ti_{15}$ alloy annealed at 1300 °C for 15 d. The white σ-Mo_5Ru_3 phase, grey β(Ti, Mo) phase and black TiRu phase are observed. The corresponding XRD result is shown in Fig.3a, in which the σ-Mo_5Ru_3 phase, β(Ti, Mo) phase and TiRu phase are clearly distinguished by the different symbols. In the $Mo_{42}Ru_{51}Ti_7$ alloy annealed at 1100 °C for 50 d, the σ-Mo_5Ru_3 phase, TiRu phase and Ru phase exist in an equilibrium, as shown in Fig.2b, while their crystal structures are confirmed by the XRD pattern in Fig.3b. Fig.2c shows a two-phase microstructure constituted by a white β(Ti, Mo) phase and a grey TiRu phase in the $Mo_{15}Ru_{39}Ti_{46}$ alloy quenched at 1300 °C. The XRD pattern shown in Fig.3c confirms the co-existence of the β(Ti, Mo) phase and the TiRu phase. Fig.2d and 2e show that the two phases of white Ru and grey TiRu are found in the $Mo_{15}Ru_{52}Ti_{33}$ alloy annealed at 1300 °C for 15 d and $Mo_{15}Ru_{60}Ti_{25}$ alloy annealed at 1100 °C for 50 d, respectively. Fig.3d shows the corresponding XRD pattern for the $Mo_{15}Ru_{60}Ti_{25}$ alloy. Fig.2f shows the two-phase equilibrium of the σ-Mo_5Ru_3 phase and TiRu phase in the 1100 °C/50 d-annealed

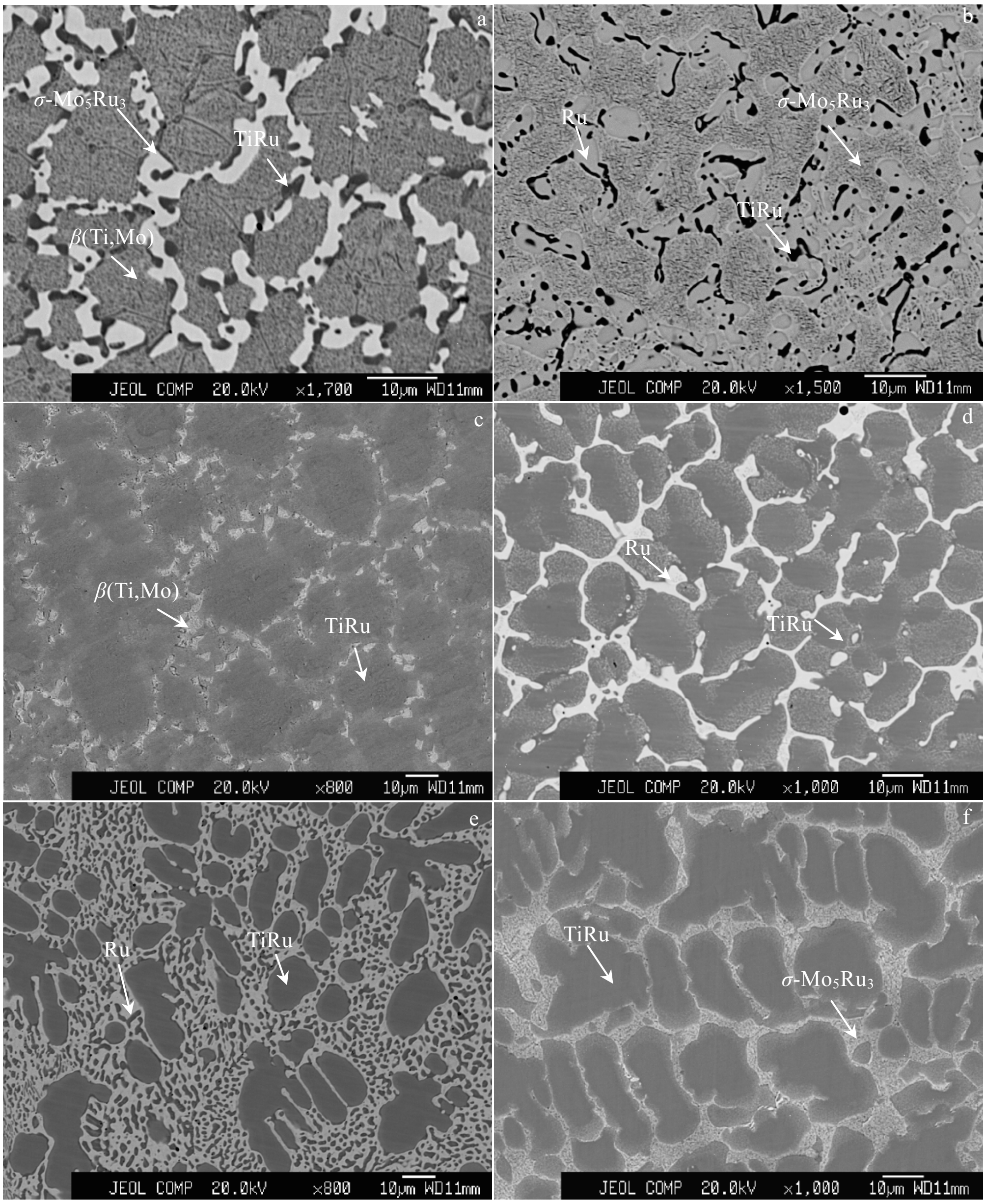

Fig.2 Back-scattered electron (BSE) images of typical ternary Mo-Ru-Ti alloys: (a) $Mo_{55}Ru_{30}Ti_{15}$ alloy annealed at 1300 °C for 15 d, (b) $Mo_{42}Ru_{51}Ti_{7}$ alloy annealed at 1100 °C for 50 d, (c) $Mo_{15}Ru_{39}Ti_{46}$ alloy annealed at 1300 °C for 15 d, (d) $Mo_{15}Ru_{52}Ti_{33}$ alloy annealed at 1300 °C for 15 d, (e) $Mo_{15}Ru_{60}Ti_{25}$ alloy annealed at 1100 °C for 50 d, and (f) $Mo_{30}Ru_{42}Ti_{28}$ alloy annealed at 1100 °C for 50 d

$Mo_{30}Ru_{42}Ti_{28}$ alloy. The white phase is σ-Mo_5Ru_3 and the grey phase is TiRu.

2.2 Isothermal sections

All the equilibrium compositions of the Mo-Ru-Ti ternary system at 1100 and 1300 °C are listed in Tables 2. Based on the experimental data mentioned above, two isothermal sections of 1100 and 1300 °C were constructed and shown in Fig.4a and 4b, respectively. The single phase, two-phase equilibrium, and three-phase equilibrium are characterized by different symbols. The determined three-phase equilibrium is represented by the solid triangles while the undetermined three-phase equilibrium is represented by the dashed triangles.

Fig.4a shows the 1100 °C isothermal section of the Mo-Ru-Ti ternary system. There are two solid solution phases of β(Ti, Mo) and Ru, and one intermetallic

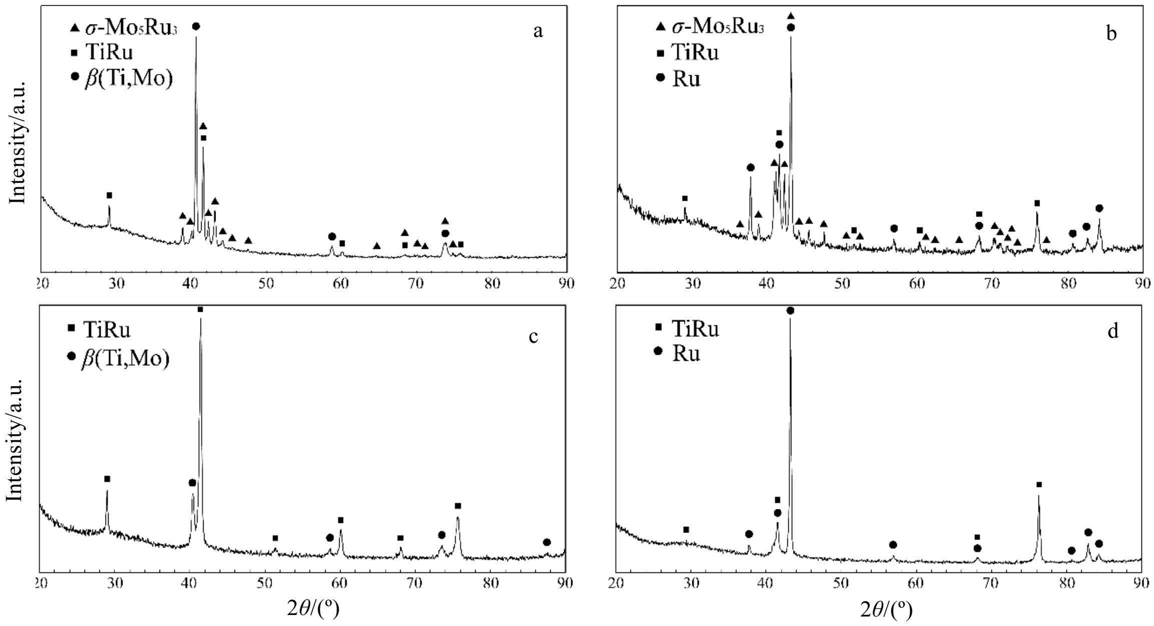

Fig.3 XRD patterns of ternary Mo-Ru-Ti alloys: (a) $Mo_{55}Ru_{30}Ti_{15}$ alloy annealed at 1300 °C for 15 d, (b) $Mo_{42}Ru_{51}Ti_7$ alloy annealed at 1100 °C for 50 d, (c) $Mo_{15}Ru_{39}Ti_{46}$ alloy annealed at 1300 °C for 15 d, and (d) $Mo_{15}Ru_{60}Ti_{25}$ alloy annealed at 1100 °C for 50 d

Table 2 Equilibrium composition of the Mo-Ru-Ti ternary system determined in the present work

Temperature/°C	Nominal alloys	Annealing Time/d	Phase equilibrium	Composition/at%					
			Phase 1/Phase 2/Phase 3	Phase 1		Phase 2		Phase 3	
				Mo	Ti	Mo	Ti	Mo	Ti
1100	$Mo_{15}Ru_{39}Ti_{46}$	50	β(Ti, Mo)/TiRu	50.1	32.6	6.4	49.9		
	$Mo_{15}Ru_{52}Ti_{33}$	50	Ru/TiRu	35.9	5.1	5.6	45.4		
	$Mo_{15}Ru_{60}Ti_{25}$	50	Ru/TiRu	26.4	3.9	2.6	47.3		
	$Mo_{30}Ru_{42}Ti_{28}$	50	σ-Mo_5Ru_3/TiRu	57.5	3.3	14.6	40.8		
	$Mo_{43}Ru_{42}Ti_{15}$	50	σ-Mo_5Ru_3/TiRu	57.2	3.2	10.3	42.3		
	$Mo_{25}Ru_{60}Ti_{15}$	50	Ru/TiRu	31.8	4.3	4.1	46.5		
	$Mo_{11}Ru_{40}Ti_{49}$	50	β(Ti, Mo)/TiRu	39.9	41.8	4.3	51.3		
	$Mo_{55}Ru_{30}Ti_{15}$	50	σ-Mo_5Ru_3/β(Ti, Mo)/TiRu	60.1	2.5	68.7	12.1	21.2	37.7
	$Mo_{61}Ru_{38}Ti_1$	50	σ-Mo_5Ru_3	60.2	0.9				
	$Mo_{42}Ru_{51}Ti_7$	50	Ru/σ-Mo_5Ru_3/TiRu	39.9	2.1	57.4	2.0	8.0	43.7
1300	$Mo_{15}Ru_{39}Ti_{46}$	15	β(Ti, Mo)/TiRu	45.9	33.5	5.1	49.2		
	$Mo_{15}Ru_{52}Ti_{33}$	15	Ru/TiRu	37.5	2.7	4.5	46.9		
	$Mo_{15}Ru_{60}Ti_{25}$	15	Ru/TiRu	27.1	3.0	1.6	48.5		
	$Mo_{30}Ru_{42}Ti_{28}$	15	σ-Mo_5Ru_3/TiRu	57.2	3.6	14.9	41.3		
	$Mo_{43}Ru_{42}Ti_{15}$	15	σ-Mo_5Ru_3/TiRu	57.1	2.8	10.4	43.3		
	$Mo_{25}Ru_{60}Ti_{15}$	15	Ru/TiRu	32.5	2.4	2.8	48.9		
	$Mo_{11}Ru_{40}Ti_{49}$	15	β(Ti, Mo)/TiRu	38.5	41.1	2.9	50.8		
	$Mo_{55}Ru_{30}Ti_{15}$	15	σ-Mo_5Ru_3/β(Ti, Mo)/TiRu	58.8	2.9	69.9	13.1	21.7	37.4
	$Mo_{61}Ru_{38}Ti_1$	15	σ-Mo_5Ru_3	59.8	1.2				
	$Mo_{42}Ru_{51}Ti_7$	15	Ru/σ-Mo_5Ru_3/TiRu	39.8	1.5	57.8	1.3	6.4	45.6

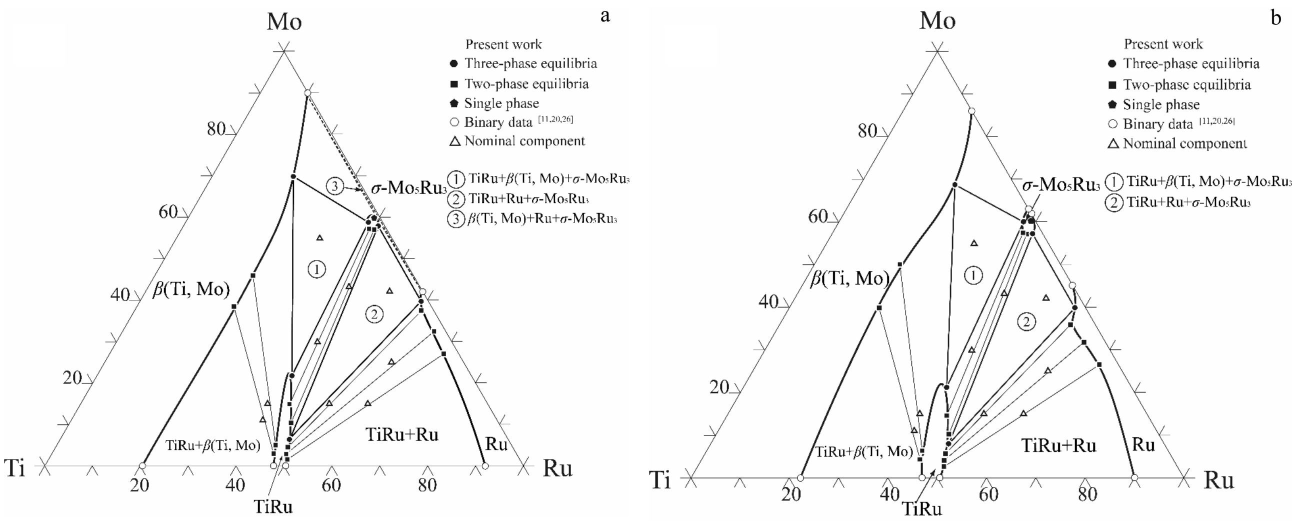

Fig.4 Experimentally determined isothermal section of Mo-Ru-Ti system at 1100 °C (a) and 1300 °C (b)

compound phase TiRu. It is worth mentioning that the σ-Mo_5Ru_3 is absent below 1141 °C in the Mo-Ru binary system. However, the σ-Mo_5Ru_3 phase exists as a stable phase at the 1100 °C isothermal section with the addition of Ti to Mo-Ru alloys. It suggests that Ti is an important element which can stabilize the σ-Mo_5Ru_3 phase against low temperature. Two three-phase regions including σ-Mo_5Ru_3+β(Ti, Mo)+TiRu and Ru+σ-Mo_5Ru_3+TiRu are determined by the $Mo_{55}Ru_{30}Ta_{15}$ and $Mo_{42}Ru_{51}Ta_7$ alloys, respectively. Another three-phase region of β(Ti, Mo)+Ru+σ-Mo_5Ru_3 is not determined. The solubility of Mo in the TiRu phase is measured to be about 21.2 at% while the solubility of Ti in the σ-Mo_5Ru_3 phase is measured to be about 3.3 at%. The β(Ti, Mo) phase forms a large continuous solid solution and extends from the Mo-rich side to the Ti-rich side. The solubility of Ru in the β(Ti, Mo) phase is roughly 19.2 at%.

Fig.4b shows the isothermal section at 1300 °C. The σ-Mo_5Ru_3 phase exists at 1300 °C in the Mo-Ru binary system, so it is present at 1300 °C isothermal section too. Thus, there is one less three-phase region of β(Ti, Mo)+Ru+σ-Mo_5Ru_3 at 1300 °C than at 1100 °C. Two three-phase regions of the σ-Mo_5Ru_3+β(Ti, Mo)+TiRu and Ru+σ-Mo_5Ru_3+TiRu are also experimentally confirmed. Compared to the 1100 °C isothermal section, the two three-phase regions at 1300 °C are both smaller. The solubility of Ti in the σ-Mo_5Ru_3 phase is about 3.6 at% and the solubility of Mo in the TiRu phase is about 21.7 at%, a bit larger than those at 1100 °C. The β(Ti, Mo) phase dissolves about 20.6 at% Ru, which is also larger compared to 1100 °C.

3 Conclusions

1) There are three three-phase regions at 1100 °C isothermal section and two three-phase regions at 1300 °C isothermal section.

2) The β(Ti, Mo) phase has a large continuous solid solution and extends from the Mo-rich side to the Ti-rich side.

3) The σ-Mo_5Ru_3 phase which dissolves a little Ti is stabilized at lower temperature due to the addition of Ti.

4) The solubility of Mo in the TiRu phase and that of Ti in the σ-Mo_5Ru_3 phase change little from 1100 °C to 1300 °C, and no ternary compound can be found.

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Mo-Ru-Ti 三元系相平衡的实验研究

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摘　要：利用电子探针成分分析和X射线衍射分析等技术建立了Mo-Ru-Ti三元系的1100和1300 ℃等温截面相图。结果表明：在1100 ℃等温截面相图中存在3个三相区，而1300 ℃等温截面相图中存在2个三相区；在1100 ℃等温截面中，由于Ti的加入，σ-Mo_5Ru_3相被稳定化并形成一个小单相区；在1100和1300 ℃等温截面相图中，β(Ti, Mo)相均从富Mo侧一直延伸至富Ti侧，并且具有较大的固溶度。Mo-Ru-Ti三元系相平衡的测定为Ti基合金热力学数据库的建立提供了基础理论信息。

关键词：Mo-Ru-Ti；相图；钛合金；电子探针分析

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